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Molybdenum sulfide/citric acid composite membrane-coated long period fiber grating sensor for measuring trace hydrogen sulfide gas

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ABSTRACT

A molybdenum sulfide/citric acid composite membrane-coated long period fiber grating (LPFG) sensor was demonstrated and applied to detect the trace hydrogen sulfide gas. The sensor was fabricated by growing molybdenum sulfide/citric acid composite film on the surface of optical fiber grating by using the sol-gel and dip-coating techniques. The sensor measures the hydrogen sulfide concentration by monitoring the molecular adsorption-induced resonant wavelength shift of LPFG in near infrared (~1555 nm) region. Experimental results show that with the increasing concentration of hydrogen sulfide, the transmission spectrum appears blue shift with time response of 89 s. In addition, a high sensitivity of 10.52 pm/ppm and a good linear relationship are achieved within a measurement range from 0 to 70 ppm. Furthermore, there is an excellent selectivity for H_2S, which has also been confirmed by the surface adsorption energy results of molybdenum sulfide with five common gases in the air (H_2S, N_2, CO_2, O_2 and Ar) based on the density functional theory calculations. The proposed sensor has an excellent detection limit of hydrogen sulfide which is as low as 0.5 ppm. This sensor has the advantages of simple structure, easy manufacture, high sensitivity and low cost, and can be used in hydrogen sulfide gas sensing places such as factories, sewers, and so on.

1. Introduction

Hydrogen sulfide, with the formula H_2S, is one of the main exhaust gases in modern industry, which is well known as a very poisonous, corrosive, flammable, and explosive gas [1–3]. More than 70 occupations have the chance to access to H_2S. It's very common to be reported on H_2S poisoning of workers. According to US health exposure limits [4,5], a lot of personal safety gas detectors, for example, those used by sewage, petrochemical and utility workers, are set to alarm at 5–10 ppm and to go into high alert at 15 ppm. In fact, 320–530 ppm of H_2S will lead to pulmonary edema with the possibility of death [6,7]. Moreover, H_2S will also cause serious environmental pollution and equipment corrosion [8]. Thus, in order to prevent the pollution and toxic accidents, it is urgent and important to propose an effective method of monitoring H_2S.

For the detection technology of hydrogen sulfide, several sensing principles have been proposed, such as conductometry [9], amperometry [10,11], potentiometry [12], and optical measurement [13,14], etc (see Table 1). Generally, the resistance-type sensors require work at high temperature and the current signal, which is not suitable for low temperature and electricity unavailable environment, such as inflammable and explosive warehouse, mine, and weapons, etc. But optical fiber sensors can overcome the above problems, i.e., optical gas sensor employs a waveguide plus coating, which measures the change of the light property when analytes gas interacts with the light during adsorption.

As far as gas sensing materials are concerned, molybdenum sulfide (MoS_2), because of its special band gap, has been widely used in many fields, such as transistor, catalyst, energy reserves, and so on [15–17]. Furthermore, MoS_2 provides large surface area which results in the strong absorption ability for gas molecules, and also has a bright application prospect in gas detection devices. As a film-forming organic dispersing agent, citric acid, having the chemical formula $C_6H_8O_7$, is a weak organic tricarboxylic acid [18]. In materials' preparation, the sol-gel process is an effective method for producing membranes from small molecules [19,20]. During the synthetic process, other compounds such as MoS_2 are introduced into the citric acid. The formation of citric complexes is believed to balance the difference in individual behaviour of these compound particles in membrane, which results in a better distribution of these particles. What's more, long period fiber grating

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Table 1
Comparison of several H_2S detection methods.

Sensor type	Sensing principle	Materials	Detection limit	Reference
Semiconductor	Conductivity impedance	CeO_2–SnO_2 thin films	1 ppm	[9]
Solid electrolyte	Amperometry/Potentiometry	Diethyl-*p*-phenylenediamine with sulfide, Silicone/Polymer film	10 ppm, 30 ppm/20 ppm	[10–12]
Optical fiber	Absorption/Fluorescence	Hollow-core photonic bandgap fiber/Cadmium oxide doped porous silica optical fiber	10 ppm/100 ppm	[13,14]

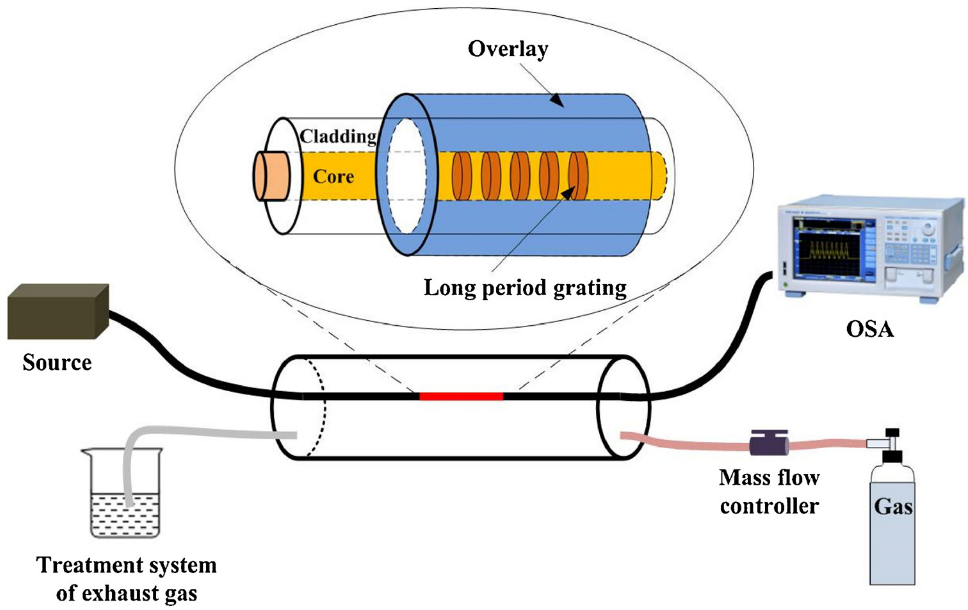

Fig. 1. Schematic diagram of the experimental setup. The inset shows the schematic diagram of LPFG structure.

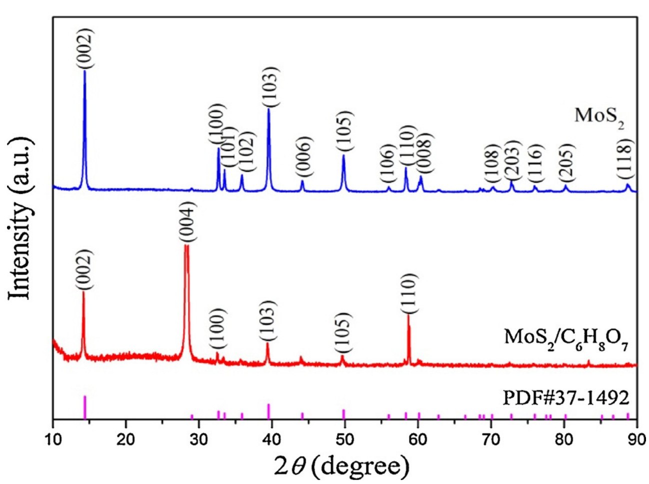

Fig. 2. XRD patterns of MoS_2 and $MoS_2/C_6H_8O_7$ membrane.

(LPFG) is widely used as fiber gas sensor with photo-induced periodic modulation of the refractive index (RI) of the fiber core [21]. A nanolayer is deposited onto the fiber which can increase the sensitivity of the LPFG [22], for example, the LPFG coated with polyelectrolyte multilayers of poly(allylamine hydrochloride)/poly-(sodium-*p*-styrenesulfonate) was successfully applied to measure a series of concentrations of sucrose solutions [23]. What's more, a multilayer film of poly(diallyldimethyammonium chloride) and tetrakis (4-sulfophenyl) porphine was coated in the surface of cladding of LPFG, and the experimental results exhibited an excellent sensitivity for ammonia gas [24]. Inspired by the above studies, in this work, a hydrogen sulfide gas sensor based on molybdenum sulfide/citric acid nano-membrane coated LPFG is fabricated and evaluated. The nano-composite film is deposited on the surface of LPFG by a sol-gel and dip-coating method. The selectivity of five gases has been investigated. The characteristic wavelength's shift of resonance band is also obtained experimentally. Meanwhile, the response characteristic of the RI of the film to hydrogen sulfide is analyzed. Utilizing the surface absorption energy of MoS_2, the hydrogen sulfide sensing property is explained by density functional calculations. The results are discussed.

2. Theory

LPFG has the ability to couple energy from the core mode to different cladding modes with the same propagation direction [21]. The difference between the propagation constant of the guided mode and the phase-matching vector of the grating equals the propagation constant of one or more cladding modes at appropriate wavelengths which correspond to a cladding mode order [25]. The phase-matching condition between the fundamental mode and the forward propagating cladding mode is given as

$$\lambda_m = (n_{co} - n_{cl}^m)\Lambda \quad (1)$$

where λ_m is the dip wavelength of the resonance band between the core and cladding modes, n_{co} and n_{cl}^m are the effective refractive indexes of the core mode and the m^{th}-order cladding mode, respectively, and Λ is the grating period which is a fixed value. When the sensor is exposed to a certain concentration of gas, the coating of the sensor will absorb a certain amount of gas molecules, resulting in changes in the RI of the cladding. According to Eq. No. (1), n_{cl}^m will change but n_{co} is invariable. Thus, the difference between n_{co} and n_{cl}^m will also change, and then lead to the resonant wavelength (λ_m) shift in the transmission spectrum of the LPFG.